

Mercury Residues in Soil Around a Large
Coal-Fired Power Plant

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Mercury Residues in Soil around a Large Coal-Fired Power Plant

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Seventy soil samples were collected on a radial grid around the Four Corners power plant. The soil samples were analyzed for total mercury using a Zeeman atomic absorption spectrophotometer. Even though the plant emits 1-2% of all the mercury released by U.S. coal-fired utilities, the soil residue levels near the plant were low and did not differ statistically from background. Relatively high concentrations were found in the samples taken west of the plant near the fly ash ponds and just east of the plant. While the fate of mercury emitted by the plant is not yet known, it is not accumulating in the soil surrounding the plant's environs.

The toxicity and hazards of mercury are well established and its distribution throughout the environment has been documented (1). Due to the known hazards, a number of reports have focused on the sources of mercury resulting from man's activities. The combustion of coal is often cited as a significant mercury source and various emission estimates have been calculated (2-4).

The amount of mercury released to the atmosphere by coal-fired electric utilities can be estimated from the amount of coal consumed using the average mercury content of the coal and a release factor. Coal combustion by the electric utilities in the United States was about 365×10^9 kg in 1975, and is projected to increase to 854×10^9 kg by the year 2000 (5). The mercury level in U.S. coal has been estimated from different data bases to average 1000 ng/g (3), 300 ng/g (4), 200 ng/g (2), and 150 ng/g (6). The latter figure, representing the most recent data, was compiled from the largest data base and is probably the best estimate. Not all mercury in coal is released during combustion and a reasonable atmosphere release factor appears to be 0.9 (7-9). Therefore, the 1975 estimated mercury release from U.S. coal-fired electric utilities totalled about 49 000 kg.

The fate of this released mercury has not been extensively studied. Klein and Russell (10) studied heavy metal fallout around a 650-MW coal-fired power plant equipped with a 120-m stack. They state that the soils around the plant are enriched in mercury, but present no statistical proof. Bolton et al. (9) conducted a major study of trace elements at the 870-MW coal-fired Allen Steam Plant and found no significant evidence of elemental accumulation. Cannon and Anderson (11) reported on elements around the Four Corners Power Plant in New Mexico, but showed no significant elevation of mercury levels in plants or soil. The lack of statistical treatment, the small number of samples involved, and the terrain and background levels of mercury limit the usefulness of these studies. For these reasons, and as a part of a project to select a biological monitor, an investigation was conducted to determine whether a mercury gradient exists around coal-fired power plants.

The selection of a power plant was based upon the estimated potential for contamination. This report focuses on the soil sampling portion of this study. All samples were collected in December 1974.

The Four Corners Power Plant was selected because of its size (>2150 MW), its coal consumption (6.3×10^9 kg/yr), its length of operation (since 1963), and its relatively short stacks (two are 76 m and two are 91 m). In addition, the surrounding arid terrain (15 to 20 cm/yr precipitation) is undisturbed by

cultivation and the soils are low in most elements including mercury (11).

Estimates of the mercury concentration of the coal burned by the plant vary considerably. Based upon a very limited sampling, Billings et al. (7) estimated the mercury concentration to be 300 ng/g. Green and Robinson (12) sampled five coal blending piles as well as the mine and found the average mercury concentration to be 375 ng/g. However, the U.S. Geological Survey analyzed 21 coal samples from the mine and reported an average value of 60 ± 20 ng/g (13). The latter analyses were made using accepted modern methods, although it was recognized that the analyses might be slightly low owing to mercury loss during drying and grinding. Thirteen samples of Four Corners coal were also analyzed by the Lawrence Radiation Laboratory for mercury. The concentrations varied from 67 to 390 ng/g with a mean of 179 ng/g (14). Data presented by the Arizona Public Service show 80 ng/g of mercury in the coal. If the true mean of these data is assumed to be between 100 and 200 ng/g, it can be calculated that the Four Corners Power Plant emitted roughly 1-2% of all mercury released by coal-fired power plants in the United States for 1974.

Sampling and Analysis

The sampling design selected was a radial grid employing 16 evenly spaced radii and five approximately logarithmically spaced circles, concentric around the power plant (Figure 1). The radii of the circles (A-E) were 1.0, 2.9, 6.8, 14.6, and 30 km. From the 80 sites on the grid, only 70 composite soil samples were collected since some sites fell on stripped land or in the cooling pond. Each sample was a composite of 10 subsamples collected 15 m apart. The upper 1 to 2 cm of soil was collected by trowel and stored in pint glass jars.

The samples were dried at 60 °C and sieved to 10 mesh (2 mm), and 5 replicates of 150 to 200 mg were analyzed directly using an Isotope Zeeman atomic absorption spectrometer (16). The Zeeman uses a 900 °C furnace for mercury analyses and no digestion procedures are required. The geometric mean of the replicate standard deviations (a measure of analytical precision) was 1.9 ng/g with a range of 0.2 to 21 ng/g. The standard deviation of the replicates could probably have been reduced if the samples had been pulverized to homogenize the sample. Eleven percent of the samples were randomly selected and reanalyzed for quality control purposes. Of the eight re-runs, seven were within ± 1 ng/g (0-9% deviation) of the original value while the eighth was off by 7 ng/g (23% deviation).

The instrumental calibration curve was calculated by regressing nanograms of mercury in six liquid standards with the instrumental readout in millivolts. The regression was verified using a U.S. Environmental Protection Agency liquid standard and two National Bureau of Standards standard reference materials, orchard leaves (no. 1571) and coal (no. 1632). The lower limit of detection was less than 1 ng.

Results

The overall arithmetic mean for the 70 samples was 16 ng/g with a range of 6 to 45 ng/g and an overall standard deviation of 6.7 ng/g (see Table I). In testing the data for normality, significant skewness and kurtosis were detected. These deviations from normality were eliminated from all statistical

Table I. Mean Mercury Concentration in Soil by Site (ng/g)

no.	radius direction	concentric circle ^a					mean	SD
		A	B	C	D	E		
1	NNE	- ^b	6	12	10		9.3	3.1
2	NE	45	9	12	13 (14)	19	20	15
3	ENE	30 (37) ^c	13	13	11 (10)	9	15	8.4
4	E	22	11 (11)	10	11	9	13	5.3
5	ESE	21	13	10	10	12	13	4.5
6	SE	16	14	10	14	11	13	2.4
7	SSE	23	-	9	6	14	13	7.4
8	S	12 (12)	20	-	14	11	14	4.0
9	SSW	14	20	12	-	12	14	3.8
10	SW	15	26	14	21	14	18	5.3
11	WSW	27	22	23	14 (14)	21	21	4.7
12	W	20	24	15 (16)	13	12	17	5.1
13	WNW	24	23	18	22	17	21	3.1
14	NW	16	15	16	26	11	17	5.5
15	NNW	-	14 (15)	13	-	-	14	0.7
16	N	-	7	23	39	-	20	12
mean		22	16	14	15	13	16	
SD		3.7	6.3	4.4	6.8	3.7		6.7

^a Radii of circles A-E are 1.0, 2.9, 6.8, 15, and 30 km, respectively. ^b -, no sample. ^c Numbers in parentheses represent a reanalysis of the sample.

analyses by a logarithmic transformation of the data.

Initially the data were subjected to a two-way analysis of variance test using the five replicate analyses of each sample. The residual error was therefore a measure of laboratory precision only. Since the computer program could not accommodate missing samples, six of the radii were dropped from the data analysis. The analysis of variance on the ten remaining radii showed the following:

(a) A highly significant difference between circles (i.e., soil mercury levels are related to distance from the power plant).

(b) A highly significant difference between radii (i.e., soil mercury levels are related to compass direction from the power plant).

(c) A highly significant interaction effect (i.e., the type of effect due to radii varies significantly from circle to circle, or the type of effect due to circles varies significantly from radii to radii).

Attempts at subdividing the data to eliminate the interaction effects were not successful.

Since it was possible that the analytical error was insignificant relative to field sampling error, a second approach was attempted. A nested two-way analysis of variance was employed in which radii were grouped in twos or fours, which provided a residual error term composed of both analytical and field sampling errors. The grouping of radii was conducted since it was felt that small changes in compass direction would have an insignificant effect on residue levels. The results of these analyses of variance were similar to those encountered previously. Highly significant effects due to circles, radii, and interaction were again discovered. Since the interaction effect could not be eliminated, it must be concluded that the distribution of mercury residues around the plant is very complex. Therefore, no statement based on statistical analysis can be made concerning the relationship of mercury residue levels relative to direction or distance from the plant.

These results are in agreement with a study by Horton et al. (17). They detected a significant negative correlation when comparing mercury levels in soil vs. distance from the power plant. Their analysis, however, did not encounter problems with interaction.

In an attempt to discern a distribution pattern of mercury,

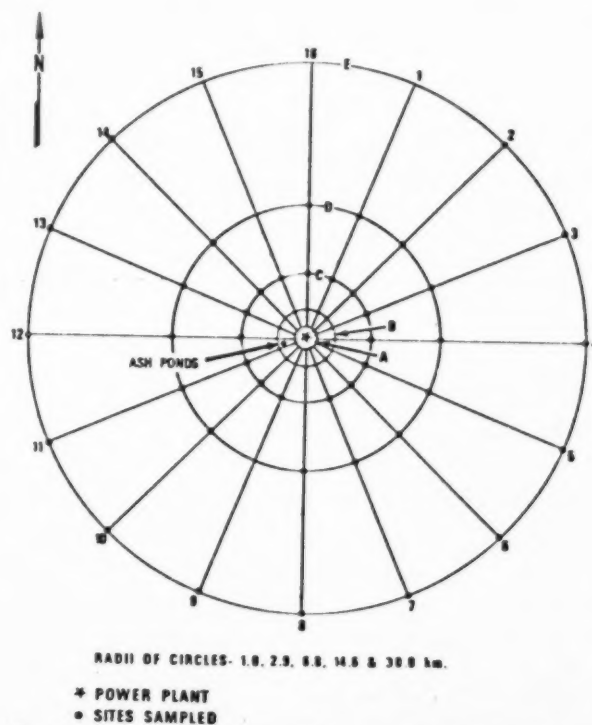


Figure 1. Soil sampling sites around the Four Corners Power Plant

a plot was made of mean mercury residues by site. Isopleths of mercury residue levels were then plotted as shown in Figure 2. Aside from a couple of small scattered sites exceeding 20 ng/g, there are three areas with levels exceeding 20 ng/g. The area due west of the plant may be related to the fly ash ponds located in this section. The 25 ng/g high to the north-northwest cannot be accounted for by the wind direction, but another power plant (350 MW, 13 k north-northeast) is located in that area. The samples with the highest mercury levels detected were collected from an undisturbed island located in the cooling pond, sites 2A and 3A.

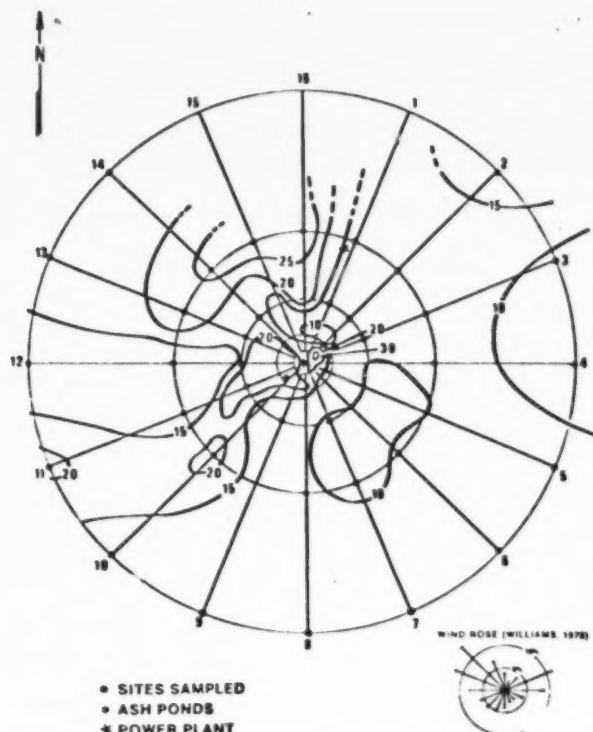


Figure 2. Distribution of mercury residues in soil around Four Corners Power Plant (ng/g)

Discussion

The 70 soil samples collected on a radial grid around the Four Corners Power Plant probably represent the most intensive sampling effort to date at that site. No statistically significant elevation of mercury residue levels was detected although some distribution patterns are evident. The levels of mercury detected are quite low, but in good agreement with soil data compiled by Cannon and Anderson (11). They reported an average value of 20 ng/g compared to 16 ng/g in this study. Shacklette et al. (19) reported the average mercury concentration in soil in the Western United States to be 83 ng/g, which is nearly twice as high as the maximum and 5 times higher than the mean value reported here.

The question then arises as to the fate of mercury emissions from the plant. The estimated annual release of mercury through stack emissions is 850 kg based upon a release factor of 0.9, a coal consumption of 6.3×10^9 kg/yr, and a mercury concentration of 150 ng/g. This value is just within Arizona Public Services' (15) emission estimate of 76 g/h plus or minus a factor of 2 for the plant operating at full load. Converting and using an operating factor of 70%, their estimate becomes 466 kg of mercury/yr. The total amount of mercury emitted by the plant since it began operating is about 6000 kg.

If all this mercury were evenly deposited within 5 or 10 km of the plant and remained in the top 2.54 cm of soil, the average soil concentration would have increased by 200 or 50 ng/g, respectively. However, the average mercury levels in soils around the power plant are considerably below these figures. These data agree with Lockeretz's deposition model (20), which indicates that the rate of mercury deposition from power plants is low compared to background rates. Apparently, the emitted mercury is being deposited over a much larger area or is being rapidly volatilized in aerobic terrestrial environments (21).

The results of this study appear to conflict with data from a recent study by Anderson and Smith (22). Their report on

coal-fired power plants states that the mercury residue levels in soils downwind from the plant are significantly higher than those upwind. This difference might, however, be due to the reported change in soil type. No evidence is presented to indicate that residue levels decrease with distance from the plant even though samples were collected from as far away as 18 km.

Conclusions

Detailed soil sampling and analyses for mercury residues indicate no significant differences in mercury residue levels in soils within 30 km of a large coal-fired power plant. These data are in general agreement with other studies which have reported little if any accumulation of mercury in soil or other media (9, 11, 20). This study fails to confirm the existence of the often cited potential problem of mercury accumulation around coal-fired power plants.

The emissions of mercury from power plants should also be compared with other sources of mercury release. Van Horn (2) indicates that U.S. coal-fired utilities emit 9% of all industrial releases to the atmosphere in the United States. Using the data of others, he also estimated that 1×10^6 kg/yr of mercury is volatilized from natural sources in the United States. From these data it was calculated that, in 1974, the emissions from coal-fired power plants amounted to about 4% of the natural degassing mercury loss.

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